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(54) Process for the Preparation of Very Pure Partially  
Fluorinated Ethanes

(72) von Halasz, Sigmar-Peter,  
Germany (Federal Republic of)

(73) Granted to Hoechst Aktiengesellschaft  
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Abstract:

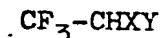
Process for the preparation of very pure partially fluorinated ethanes

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The reaction of fluorine-containing ethylenes of the formula  $\text{CF}_2=\text{CXY}$ , in which X denotes H or F and Y denotes H, F, Cl, Br or iodine, with hydrogen fluoride to form fluorine-containing ethanes of the formula  $\text{CF}_3\text{-CHXY}$  is carried out, according to the invention, at temperatures of 20 - 200°C and in the presence of a chromium oxyfluoride catalyst which has been treated with hydrogen fluoride. Only a small amount of by-products is formed in this process.

The present invention relates to a process for the preparation of very pure partially fluorinated ethanes by the hydrofluorination of fluorine-containing ethylenes.

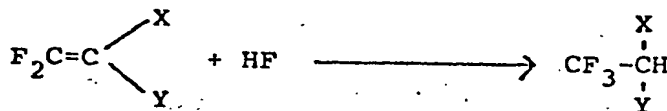
5 Because of their particular chemical and physical properties, partially fluorinated ethanes of the general formula



in which X denotes H or F and Y denotes H, F, Cl, Br or  
10 I, are suitable for use in numerous fields of application, for example as additives in gaseous analgesics and anesthetics, as heat exchange media or as components of propellants. Simple and economical processes for the preparation of representatives of this class of compounds  
15 are therefore of interest.

The said partially fluorinated ethanes are in themselves known and can be prepared by several, generally laboratory-scale, processes. If very pure fluorine-  
containing ethylenes of the general formula  $\text{CF}_2=\text{CXY}$  are  
20 available in sufficient amount, hydrofluorination in the gas phase, in the presence of a solid catalyst, is a possible method.

The addition of hydrogen fluoride onto fluorine-  
containing ethylenes, in the gas phase, with the forma-  
25 tion of partially fluorinated ethanes in accordance with the equation



has already been described for some compounds. However, all known fluorination processes in the gas phase require relatively high temperatures, generally above 250°C and in some cases even above 400°C. At these temperatures, 5 undesired side reactions necessarily result. For example, in the case of ethylenes which contain chlorine, bromine or iodine atoms, the halogen can be substituted by fluorine. Even in the partially fluorinated ethane formed, the halogen can be displaced by the fluorine of 10 the hydrogen fluoride at the high temperatures mentioned. This reactivity can be used directly for the preparation of F-substituted compounds. For example, according to U.S. Patent Specification 2,951,102, the compound  $\text{CF}_3\text{CHClF}$  is prepared from  $\text{CF}_2\text{BrCHClF}$  by reaction with 15 HF, at 300°C, on a chromium oxyfluoride catalyst.

The hydrofluorination of trifluoroethylene at reaction temperatures of 350°C is described in German Offenlegungsschrift 2,837,515. This process uses a chromium oxyfluoride catalyst which was prepared accord- 20 ing to British Patent Specification 1,307,224. The yields of 1,1,1,2-tetrafluoroethane are 90 to 95% of theory. The possible residence times lie within narrow limits and the proportion of fluorinated by-products is high.

25 Again on a chromium oxyfluoride catalyst, chloro-trifluoroethylene can be reacted at 320°C, according to U.S. Patent Specification 3,755,477, to give a mixture which inter alia contains 2-chloro-1,1,1,2-tetrafluoroethane (13% of theory). The same hydrofluorination

process is carried out at 350 to 400°C according to Canadian Patent Specification 849,024; in this process, a considerable part of the starting material is not converted.

10 In attempts by the Applicant Company to apply the known gas-phase hydrofluorination processes to the said fluorine-containing ethylenes, the following side reactions were observed: isomerizations, disproportionations, oligomerizations, polymerizations, fragmentation of the C-C bonds and also substitution, for example of chlorine or hydrogen by fluorine. These side reactions reduce the yields and lead to by-products which must then be separated off, frequently at considerable expense. On the other hand, the reaction temperatures in the known processes are uneconomically high. Thus, the life of the catalysts employed is also limited to a considerable extent, in particular when employing ethylenes which contain hydrogen, bromine or iodine and which are therefore capable of poisoning the catalyst at high temperatures.

20 The object was therefore to provide a simple, productive and environmentally harmless process for the preparation of very pure partially fluorinated ethanes, which can be carried out at the lowest possible temperatures, which proceeds with high selectivity and with high yields, that is to say in which the known side reactions are not involved, and which can easily be applied continuously.

The present invention provides a process for the preparation of very pure fluorine-containing ethanes of the general formula  $\text{CF}_3\text{-CHXY}$ , in which X denotes H or F and Y denotes H, F, Cl, Br or iodine, from fluorine-containing ethylenes of the general formula  $\text{CF}_2\text{=CXY}$ , in which X and Y

have the meaning indicated above, with at least the equimolar amount of hydrogen fluoride, in the gas phase, which process comprises carrying out the reaction at temperatures of 20-200°C and in the presence of a chromium oxyfluoride catalyst which has been treated with hydrogen fluoride and elemental fluorine.

10 The chromium oxyfluoride catalyst, treated with hydrogen fluoride, which is employed in the process according to the invention can be prepared, for example, by reacting hydrated chromium oxides with hydrogen fluoride (according to German Auslegeschrift 1,252,182) or by heating hydrated chromium trifluoride in the presence of oxygen (United States Patent Specification 2,745,886).

20 Those catalysts which are obtained from hydrated chromium oxide by treatment with hydrogen fluoride only require an after-treatment with hydrogen fluoride when they are employed after a relatively long time, for example after a few months, for the process according to the invention. However, if the same catalysts are used immediately after they have been prepared, an after-treatment with hydrogen fluoride is unnecessary. In the case of the catalysts prepared from chromium trifluoride, however, the after-treatment with hydrogen fluoride is always necessary.

The after-treatment of the chromium oxyfluoride

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catalysts is carried out either for a relatively long time (more than 48 hours) with hydrogen fluoride, at temperatures of 250 to 300°C, or preferably for a relatively short time (about 5 to 10 hours) with a gas mixture which contains hydrogen fluoride and elementary fluorine. In this process, elementary fluorine is generally diluted with an inert gas and anhydrous hydrogen fluoride and passed into a tube filled with the chromium oxyfluoride catalyst and heated to temperatures of 150 to 210°C. The activation time depends on the history of the catalyst and is generally 5 to 10 hours. Advantageously, the flow rate per liter of catalyst is 0.1 to 5.0 liters/hour for the fluorine metered in, 1.0 to 3.0 liters/hour for the inert gas and 10 to 50 g/hour for the hydrogen fluoride. Of course, the treatment with hydrogen fluoride/fluorine can be carried out by passing the latter not only simultaneously but also in succession.

The treatment of a chromium oxyfluoride catalyst with a mixture of hydrogen fluoride and elementary fluorine is substantially known from German Offenlegungsschrift 2,702,360 and is used in this case for the re-activation of catalysts which are employed for chlorine/fluorine exchange reactions.

The process according to the invention is generally carried out in the manner of a customary catalytic gas/solid reaction by passing a gas mixture, consisting of the fluorine-containing ethylene to be reacted and of hydrogen fluoride, through a heatable reaction

tube which is filled with the abovementioned pre-treated chromium oxyfluoride catalyst. The reaction tube is preferably arranged vertically.

The reaction tube consists of a material, such as nickel, steel, copper or platinum, which is sufficiently resistant towards hydrogen fluoride and elementary fluorine, or is provided with a suitable lining, for example of polytetrafluoroethylene or another suitable highly fluorinated polymer. The reaction gases which leave the reaction tube are freed of excess hydrogen fluoride by washing with water or by absorption in towers containing granular sodium fluoride. The partially fluorinated ethane purified beforehand in this way is condensed in suitable cooling traps.

The shape of the chromium oxyfluoride catalyst employed is not critical; spheres, cubes or cylinders having a volume of 0.01 to 10 cc are customarily used.

The use of the compounds trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene or trifluoroiodoethylene is preferred in the process according to the invention. This gives, respectively, 1,1,1,2-tetrafluoroethane, pentafluoroethane, 2-chloro-1,1,1,2-tetrafluoroethane, 1-bromo-1,2,2,2-tetrafluoroethane or 1,2,2,2-tetrafluoro-1-iodo-ethane in approximately quantitative yields.

To carry out the process according to the invention, the fluorine-containing ethylenes, in the gaseous state, are first mixed with hydrogen fluoride and then passed into the reactor filled with the catalyst.



The boiling points of a few starting materials are listed in the following table:

Table 1

	Fluorine-containing ethylene	Formula	Boiling point/1 bar
5	1,1-Difluoroethylene	$\text{CF}_2=\text{CH}_2$	$-82^\circ\text{C}$
	Trifluoroethylene	$\text{CF}_2=\text{CHF}$	$-61^\circ\text{C}$
	2-Chloro-1,1-difluoroethylene	$\text{CF}_2=\text{CHCl}$	$-17.7^\circ\text{C}$
10	1-Bromo-2,2-difluoroethylene	$\text{CF}_2=\text{CHBr}$	$+ 6.1^\circ\text{C}$
	2,2-Difluoro-1-iodo-ethylene	$\text{CF}_2=\text{CHI}$	$+ 34^\circ\text{C}$
	Tetrafluoroethylene	$\text{CF}_2=\text{CF}_2$	$-76.3^\circ\text{C}$
15	Chlorotrifluoroethylene	$\text{CF}_2=\text{CFCl}$	$-27.9^\circ\text{C}$
	Bromotrifluoroethylene	$\text{CF}_2=\text{CFBr}$	$- 4.5^\circ\text{C}$
20	Trifluoroiodoethylene	$\text{CF}_2=\text{CFI}$	$+ 29^\circ\text{C}$

The fluorine-containing ethylenes generally used are of technical purity and are advantageously as anhydrous as possible. These starting materials can be prepared in an easy manner by processes which are in themselves known; some representatives, such as, for example, tetrafluoroethylene, chlorotrifluoroethylene or 1,1-difluoroethylene, are also available on an industrial scale.

At atmospheric pressure, the throughput of fluorine-containing ethylenes is advantageously about 1 to 90 liters (about 0.04 to 4 moles) per liter of cata-

lyst and per hour. At higher pressures, the throughput of fluorine-containing ethylenes can be correspondingly higher. Lower throughputs are possible but uneconomical.

5       The process according to the invention generally takes place at normal pressure, but also permits the application of excess pressure or reduced pressure within wide limits. Thus, the reaction can be carried out at pressures of less than 1 bar or also at an excess pressure of 1 to 10 bars or more, preferably at 1 to 3 bars. 10 The application of excess pressure is preferable, especially for achieving high space-time yields.

      If the starting compounds are not anhydrous, side reactions (formation of oxygen-containing products) can 15 result.

      Hydrogen fluoride is generally added without dilution. The amount of hydrogen fluoride metered in in the gaseous state is generally between 0.8 and 250 g (0.04 and 12.5 moles respectively) per liter of catalyst 20 and per hour. It should be at least equivalent to, but preferably greater than, the amount of the particular fluorine-containing ethylene employed. The molar ratio of fluorine-containing ethylene to hydrogen fluoride is generally between 1:3 and 1:1, preferably between 1:2 25 and 1:1.1 and especially between 1:1.5 and 1:1.1. The total amount of hydrogen fluoride passed in is not critical provided that only an excess (relative to the fluorine-containing ethylene employed) is used. An excess of hydrogen fluoride is favorable inasmuch as a quantitative

conversion of the fluorine-containing ethylene is thereby achieved. Relatively large excesses of hydrogen fluoride are also possible; however, this increases the expense involved in the working-up. Excess hydrogen fluoride is either removed from the reaction gas by washing with water or dilute sodium hydroxide solution or is absorbed at room temperature in towers containing granular sodium fluoride. Because the hydrogen fluoride can be thermally desorbed again after absorption on sodium fluoride and can be re-employed, the losses of hydrogen fluoride remain very small with this procedure. Working-up by fractional distillation is also possible.

In general, the reaction is carried out without the addition of an inert gas. Although dilution, for example with nitrogen or another inert gas, is possible, it only brings about a minimal increase in the yield.

The reactions are carried out at temperatures of 20 to 200°C, advantageously at 40 to 190°C and especially at 60 to 180°C.

The residence time of fluorine-containing ethylene, or of the fluorine-containing ethane formed therefrom, in the reactor is not critical. In both cases, it can vary between a few seconds and a few minutes; it only has an upper limit as a result of economic considerations. It is to be regarded as a particular advantage of the process according to the invention that the residence time can be varied within wide limits without the composition of the reaction product being influenced thereby.

With the process according to the invention, a continuous procedure, that is to say continuous passage of the starting materials, continuous recycling of the excess hydrogen fluoride and also continuous isolation  
5 of the partially fluorinated ethane formed, is easily possible. Particular advantages of the continuous procedure lie in the good utilization of the starting materials employed and in the small amount of effluent and off-gas formed.

10 With the process according to the invention, the conversion of the fluorine-containing ethylenes employed is generally more than 95%, but frequently 99 - 100%.

Because of the high selectivity of the process according to the invention, the yields of partially  
15 fluorinated ethanes are likewise more than 95%, but frequently more than 98%. The ethanes are thus obtained in high purity. The process according to the invention proves advantageous above all insofar as side reactions are virtually completely suppressed and the  
20 working-up consequently proves exceptionally simple.

The following table shows the boiling points of the partially fluorinated ethanes which can be prepared from the fluorine-containing ethylenes of Table 1.

Table 2: Ethanes

Name	Formula	Boiling point/1 bar
1,1,1-Trifluoroethane	$\text{CF}_3\text{-CH}_3$	$-47.8^\circ\text{C}$
5 1,1,1,2-Tetrafluoroethane	$\text{CF}_3\text{-CH}_2\text{F}$	$-26.5^\circ\text{C}$
2-Chloro-1,1,1-trifluoroethane	$\text{CF}_3\text{-CH}_2\text{Cl}$	$+6.1^\circ\text{C}$
1-Bromo-2,2,2-trifluoroethane	$\text{CF}_3\text{-CH}_2\text{Br}$	$+26^\circ\text{C}$
2,2,2-Trifluoro-1-iodo-ethane	$\text{CF}_3\text{-CH}_2\text{I}$	$+55^\circ\text{C}$
Pentafluoroethane	$\text{CF}_3\text{-CHF}_2$	$-48.5^\circ\text{C}$
10 2-Chloro-1,1,1,2-tetrafluoro-ethane	$\text{CF}_3\text{-CHClF}$	$-12^\circ\text{C}$
1-Bromo-1,2,2,2-tetrafluoro-ethane	$\text{CF}_3\text{-CHBrF}$	$+7^\circ\text{C}$
15 1,2,2,2-Tetrafluoro-1-iodo-ethane	$\text{CF}_3\text{-CHI}$	$+39^\circ\text{C}$

It is known from German Offenlegungsschrift 2,712,732 that perfluoropropylene reacts with hydrogen fluoride at temperatures of 100 to  $350^\circ\text{C}$ , in the presence of chromium oxyfluoride catalysts. In this reaction, the yields of 2H-heptafluoropropane, at reaction temperatures below  $200^\circ\text{C}$ , are only moderate. For example, at 160 to  $170^\circ\text{C}$ , they are only 82% of theory. Moreover, the significance of the pre-treatment of the catalyst with hydrogen fluoride is not evident from this literature reference.

It is surprising that, in the presence of the chromium oxyfluoride catalysts subjected to an after-treatment with HF, the hydrofluorination of fluorine-containing ethylenes proceeds with high conversions, which are frequently quantitative, and with exceptionally

high selectivity. It is particularly surprising that the reaction temperatures of the process according to the invention are unexpectedly low, in comparison with the state of the art.

5           The process according to the invention represents a considerable technical advance because it permits the preparation of partially fluorinated ethanes in yields of more than 95%, in some cases up to 99%, starting from the fluorine-containing ethylenes, which are either  
10 obtainable industrially or are readily accessible via other industrial intermediates, with optimum utilization of the starting materials, without substantial formation of the customary isomerization products, disproportiona-  
tion products, oligomerization products, polymerization  
15 products, fragmentation products or substitution products. As a consequence of this, working-up is simple and a high degree of purity of the end products can easily be achieved. Furthermore, the process according to the  
invention is of great interest because of the low reac-  
20 tion temperatures and the consequent long life of the catalysts employed.

The process is illustrated in greater detail by the following examples:

Example 1

25           The activation of the chromium oxyfluoride catalysts with hydrogen fluoride or with a gas mixture of hydrogen fluoride and elementary fluorine, and the subsequent hydrofluorination of the fluorine-containing ethylenes, were carried out in the same pilot plant.

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This consists of a vertically standing nickel tube having a length of 150 cm and an internal diameter of 5 cm. The reactor is heated externally with a heating mantle; a VA-steel tube having an external diameter of 0.6 cm, an internal diameter of 0.4 cm and a length of 145 cm, through which a thermocouple for measuring the internal temperature can be introduced at any desired level of the reactor, runs axially through the inside of the reactor tube. The granular catalyst material is kept at the desired level of the tube by means of a sieve part mounted inside the reaction tube. At the lower end of the reactor, there is a nickel evaporation vessel which can be heated separately, into which the lines for gaseous hydrogen fluoride, diluted or undiluted fluorine gas and the gaseous fluorine-containing ethylene (in Example 1: 1,1-difluoroethylene) lead. The evaporation vessel is kept at a temperature between the boiling point of hydrogen fluoride (+20°C) and the reactor temperature. From the upper end of the nickel reactor, a line leads into a washing receiver filled with water, in which receiver hydrogen fluoride which has not reacted in the hydrofluorination is trapped and sampled by titration. During the activation with elementary fluorine, a receiver containing hexafluoropropene trimer is inserted between the reactor outlet and the washing vessel. Excess fluorine can thus be absorbed without danger (compare German Offenlegungsschrift 2,332,097); additional fluorine tests are carried out during the activation with potassium

iodide paper.

Elementary fluorine ( $F_2$ ) is taken from a commercially available steel cylinder, measured with a pre-calibrated differential pressure flowmeter, diluted with  
5 nitrogen and passed into the reactor. A riser manometer for observing the back pressure which develops is fitted upstream of the fluorine flowmeter and simultaneously serves as a safety valve. The back-pressure meters are filled with perfluorinated polyether oils.

10 The hydrogen fluoride (HF) employed has the commercially available purity of more than 99% and is metered using a measuring arrangement which is basically similar to that described for the fluorine. Radiant heaters are additionally fitted in order to prevent HF  
15 from condensing in the lines up to the evaporator.

600 ml (bulk volume) of a chromium oxyfluoride catalyst which has been prepared by fluorinating hydrated chromium sesquioxide with hydrogen fluoride according to German Auslegeschrift 1,252,182 are initially intro-  
20 duced into the reactor tube. The catalyst initially introduced is activated by treatment, at an internal temperature of  $190^{\circ}C$ , for 10 hours, with a gas mixture consisting of 0.35 liter/hour of fluorine, 0.5 liter/hour of nitrogen and 15 g/hour of hydrogen fluoride; it is  
25 then flushed with 15 g/hour of hydrogen fluoride at the same internal temperature, for 5 hours.

The 1,1-difluoroethylene is taken from a commercially available steel cylinder. For hydrofluorination, a total of 420 g (6.56 moles) of  $CF_2=CH_2$  and 237 g



(11.85 moles) of HF, corresponding to a molar ratio  $\text{CF}_2=\text{CH}_2:\text{HF}$  of 1:1.81, are passed in over the activated chromium oxyfluoride catalyst, at reactor temperatures of  $80^\circ\text{C}$  (at the start) to  $98^\circ\text{C}$  (after commencement of the exothermic addition reaction), in the course of 6 hours.

5.23 moles of HF are trapped in the wash water. For drying, the gaseous reaction product is passed through a  $\text{CaCl}_2$  drying tower and then condensed in a high-efficiency trap cooled with solid carbon dioxide. Measurement of this crude product by gas chromatography on a  $\text{R}$  PORAPAK column gives the following composition:

	$\text{CF}_3-\text{CH}_3$	99.6 %
	$\text{CF}_2=\text{CH}_2$	0.3 %
15	$\text{CHF}_3$	$<0.05$ %
	$\text{CH}_2\text{F}_2$	$<0.05$ %
	$\text{CHF}_2-\text{CH}_3$	$<0.05$ %

The condensed crude product weighs 537 g. The yield of  $\text{CF}_3-\text{CH}_3$  is thus 97.3% of theory, relative to the  $\text{CF}_2=\text{CH}_2$  reacted. Further identification of 1,1,1-trifluoroethane is carried out by means of infra-red,  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra. The boiling point of the product is  $-48$  to  $-47^\circ\text{C}$ .

#### Example 2

25 Using the experimental arrangement of Example (1), trifluoroethylene is hydrofluorinated by passing a total of 235 g (2.87 moles) of  $\text{CF}_2=\text{CHF}$ , which has been prepared by dehalogenating  $\text{CBrF}_2-\text{CHClF}$ , and 85 g (4.15 moles) of HF, corresponding to a molar ratio of  $\text{CF}_2=\text{CHF}:\text{HF}$  of 1:1.45,

over the chromium oxyfluoride catalyst used in Example (1), at temperatures of 124 to 143°C, in the course of 3 hours.

In the wash water, 1.25 moles of HF are determined by titration. The gas chromatographic recording of the crude product collected in the trap gives the following values:

	$\text{CF}_3\text{-CH}_2\text{F}$	99.7 %
	$\text{CF}_2\text{=CHF}$	< 0.05 %
	$\text{CHF}_3$	< 0.05 %
10	$\text{CF}_3\text{-CH}_3$	< 0.05 %

The condensate weighs 286.5 g; the yield of 1,1,1,2-tetrafluoroethane is thus 97.6% of theory, relative to the  $\text{CF}_2\text{=CHF}$  reacted. The characterization of 1,1,1,2-tetrafluoroethane is carried out by means of IR,  $^{19}\text{F}$  and  $^1\text{H}$  NMR measurements; the boiling point is -27°C to -26°C.

#### Comparison Example 1

Using the experimental arrangement of Example (1), 600 ml (bulk volume) of a chromium oxyfluoride catalyst which has been prepared according to German Auslegeschrift 1,252,182 are initially introduced. In this case, the catalyst material is initially pre-treated only with hydrogen fluoride; in this process, a total of 1,080 g of HF are passed over the catalyst initially introduced, at a rate of 15 g/hour, at temperatures of 330°C to 350°C, in the course of 72 hours.

A total of 243 g (2.96 moles) of  $\text{CF}_2\text{=CHF}$  and 86 g (4.30 moles) of HF, corresponding to a molar ratio  $\text{CF}_2\text{=CHF:HF}$  of 1:1.45, are passed over the catalyst

prepared in the manner described, at temperatures of 125 to 142°C, in the course of 3 hours.

1.45 moles of HF are trapped in the wash water.

The condensed crude product has the following composition

5 according to measurement by gas chromatography:

$\text{CF}_3\text{-CH}_2\text{F}$	95.8 %
$\text{CF}_2\text{=CHF}$	4.0 %
$\text{CHF}_3$	< 0.05 %
$\text{CF}_3\text{CH}_3$	< 0.05 %

10 The crude product has a weight of 293.5 g; the yield of  $\text{CF}_3\text{-CH}_2\text{F}$  is thus 97% of theory, relative to the  $\text{CF}_2\text{=CHF}$  reacted, but the conversion of  $\text{CF}_2\text{=CHF}$  only reaches about 96%.

### Example 3

15 Using the experimental arrangement of Example (1), the catalyst used in Comparison Example (1) is activated, as described in Example (1), by pre-treatment with a gas mixture consisting of 0.35 liter/hour of fluorine, 0.5 liter/hour of  $\text{N}_2$  and 15 g/hour of HF, at an internal  
20 temperature of 190 to 195°C, for 10 hours. It is then flushed with 15 g/hour of HF, at 190°C, for 5 hours.

A gas mixture consisting of a total of 1,698 g (20.7 moles) of  $\text{CF}_2\text{=CHF}$  and 666 g (33.3 moles) of HF, this being a molar ratio  $\text{CF}_2\text{=CHF}:\text{HF}$  of 1:1.61, is passed  
25 over the chromium oxyfluoride catalyst prepared in the manner described, at an internal temperature of 75°C (at the start) to 96°C (caused by the heat of reaction), in the course of 26 hours.

12.55 moles of HF are found in the wash water.

Measurements by gas chromatography give the following composition for the crude product trapped:

$\text{CF}_3\text{-CH}_2\text{F}$	99.8%
$\text{CF}_2\text{=CHF}$	< 0.05%
$\text{CHF}_3$	< 0.05%
$\text{CF}_3\text{-CH}_3$	< 0.05%

The condensate weighs 2,088 g; the yield of  $\text{CF}_3\text{-CH}_2\text{F}$  is thus about 99% of theory, relative to  $\text{CF}_2\text{=CHF}$  reacted; in this example, the latter could be quantitatively converted at very moderate temperatures.

#### Example 4

Using the experimental apparatus of Example (1), a gas mixture consisting of a total of 510 g (5.18 moles) of 2-chloro-1,1-difluoroethylene, which has been prepared by dechlorinating 1,1,2-trichloro-2,2-difluoroethane, and 153 g (7.65 moles) of HF, this being a molar ratio  $\text{CF}_2\text{=CHCl:HF}$  of 1:1.48, is passed over the chromium oxyfluoride catalyst used in Example (3), at an internal temperature of 120 to 131°C, in the course of 6.0 hours.

In the wash water, 2.33 moles of HF and 0.04 mole of HCl are determined by titration. According to gas chromatographic investigations, the crude product consists of the following constituents:

$\text{CF}_3\text{-CH}_2\text{Cl}$	99.0%
$\text{CF}_2\text{=CHCl}$	< 0.05%
$\text{CF}_3\text{-CH}_2\text{F}$	0.8%
$\text{CF}_3\text{-CH}_3$	< 0.05%

The crude product trapped has a weight of 603 g;

the resulting yield of 2-chloro-1,1,1-trifluoroethane is thus 97.2% of theory, relative to the  $\text{CF}_2=\text{CHCl}$  reacted. The ethane obtained, namely  $\text{CF}_3-\text{CH}_2\text{Cl}$ , was further characterized by recording IR,  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra and also  
 5 by determining the boiling point of  $+6^\circ\text{C}$  to  $+6.5^\circ\text{C}$ .

#### Example 5

For the hydrofluorination of tetrafluoroethylene, which is employed in the high purity required for polymerizations, 600 ml (bulk volume) of chromium oxyfluoride  
 10 catalyst are pre-treated, in the apparatus used in Example (1), with a gas mixture consisting of  $\text{F}_2$ , HF and  $\text{N}_2$ , as described in Example (1).

A total of 370 g (3.70 moles) of  $\text{CF}_2=\text{CF}_2$  and 170 g (8.5 moles) of HF, corresponding to a molar ratio  
 15  $\text{CF}_2=\text{CF}_2:\text{HF}$  of 1:2.3, are passed over the catalyst pre-treated in this way, at an internal temperature of 165 to  $179^\circ\text{C}$ , in the course of 5.0 hours.

4.95 moles of HF are trapped in the wash water. Gas chromatographic analysis of the resulting crude product  
 20 gives the following values:

	$\text{CF}_3-\text{CHF}_2$	92.5 %
	$\text{CF}_2=\text{CF}_2$	6.3 %
	$\text{CHF}_3$	0.2 %
	$\text{CF}_3-\text{CF}_3$	0.25 %
25	cyclo- $\text{C}_4\text{F}_8$	~ 1 %

The resulting condensate weighs 417 g; the yield of pentafluoroethane is thus about 93% of theory, relative to the  $\text{CF}_2=\text{CF}_2$  reacted. The pentafluoroethane,  $\text{CF}_3-\text{CHF}_2$ , was further characterized by IR and NMR measurements.

Subsequent low-temperature distillation gave a fraction of 372 g in the boiling range from  $-49$  to  $-47.5^{\circ}\text{C}$ /normal pressure, consisting of over 99% of pentafluoroethane.

#### Comparison Example 2

5           Using the experimental arrangement of Example (1), filled with the chromium oxyfluoride catalyst of Example 5, a total of 202.5 g (2.03 moles) of  $\text{CF}_2=\text{CF}_2$  and 113 g (5.65 moles) of HF, corresponding to a molar ratio  $\text{CF}_2=\text{CF}_2:\text{HF}$  of 1:2.8, are reacted at a temperature of 10  $280^{\circ}\text{C}$  to  $288^{\circ}\text{C}$ , in the course of 3.0 hours.

4.05 moles of HF are determined in the wash water. Gas chromatographic measurement of the crude product trapped gives the following data:

	$\text{CF}_3-\text{CHF}_2$	83.5 %
15	$\text{CF}_2=\text{CF}_2$	< 0.05 %
	$\text{CF}_3-\text{CF}_3$	3.5 %
	cyclo- $\text{C}_4\text{F}_8$	3.3 %
	$\text{C}_6\text{F}_{12}$	8.5 %

Furthermore, white solid residues consisting of 20 polytetrafluoroethylene are observed on the catalyst material. With a weight of 184 g for the condensate (crude product), the yield of pentafluoroethane in this comparison example is only about 63% of theory, relative to the  $\text{CF}_2=\text{CF}_2$  reacted. Although an increase in the 25 reactor temperature leads to a quantitative conversion of ethylene, it gives rise to a higher proportion of by-products.

#### Example 6

For the hydrofluorination of chlorotrifluoro-

ethylene, which is easily obtainable in high purity as an industrial intermediate, the chromium oxyfluoride catalyst used in Example (4) is initially introduced into the experimental apparatus of Example (1).

At an internal temperature of 170 to 178°C, a total of 605 g (5.19 moles) of  $\text{CF}_2=\text{CFCl}$  and 152 g (7.6 moles) of HF, corresponding to a molar ratio  $\text{CF}_2=\text{CFCl}:\text{HF}$  of 1:1.46, are reacted in the reactor tube in the course of 6.5 hours.

10 2.48 moles of HF and 0.03 mole of HCl are determined in the wash water by titration. The composition of the crude condensate is determined by means of GC measurement:

$\text{CF}_3-\text{CHClF}$	95.6%
$\text{CF}_2=\text{CFCl}$	3.0%
$\text{CF}_3-\text{CHCl}_2$	0.4%
$\text{CF}_3-\text{CHF}_2$	0.8%
$\text{CF}_3-\text{CH}_2\text{Cl}$	< 0.1%
$\text{CF}_3-\text{CClF}_2$	< 0.1%

20 No polymers were observed. The crude product trapped weighs 669 g; the yield of  $\text{CF}_3-\text{CHClF}$  is thus 93.1% of theory, relative to the  $\text{CF}_2=\text{CFCl}$  reacted. Further characterization is carried out by means of IR and  $^{19}\text{F}$  and  $^1\text{H}$  NMR measurements. Subsequent low-temperature distillation at -12.5 to -11°C gives a fraction, having a weight of 612 g, of pure 2-chloro-1,1,1,2-tetrafluoroethane.

#### Comparison Example 3

Using the experimental apparatus of Example (1),

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filled with the catalyst of Comparison Example (1), a total of 354 g (3.04 moles) of  $\text{CF}_2=\text{CFCl}$  and 92 g (4.6 moles) of HF, corresponding to a molar ratio  $\text{CF}_2=\text{CFCl}:\text{HF}$  of 1:1.51, are passed through at an internal temperature of 270 to 280°C, in the course of 4 hours.

1.19 moles of HF and 0.33 mole of HCl are trapped in the wash water. The crude product has the following composition according to GC analysis:

	$\text{CF}_3-\text{CHClF}$	20.7 %
10	$\text{CF}_2=\text{CFCl}$	< 0.05 %
	(A) $\text{CF}_3-\text{CHCl}_2$	29.6 %
	(B) $\text{CF}_3-\text{CHF}_2$	41.0 %
	(C) $\text{CF}_3-\text{CH}_2\text{Cl}$	4.5 %
	(D) $\text{CF}_3-\text{CClF}_2$	4.2 %

15 The formation of the products (A) and (B) or (C) and (D) can be explained by the various possibilities of disproportionation of the  $\text{CF}_3-\text{CHClF}$  formed; the high proportion of product (B), namely pentafluoroethane, arises as a result of chlorine/fluorine exchange in the  $\text{CF}_3-\text{CHClF}$ . This comparison example clearly shows the decisive influence of the reactor temperature on the composition of the reaction products.

#### Example 7.

For the hydrofluorination of bromotrifluoro-ethylene, a gas mixture consisting of a total of 334 g (2.07 moles) of  $\text{CF}_2=\text{CFBr}$  and 110 g (5.50 moles) of HF (molar ratio  $\text{CF}_2=\text{CFBr}:\text{HF}$  of 1:2.66) is reacted in the experimental apparatus of Example (1), filled with a catalyst as described in Example (1), at a temperature of



165 to 176°C, in the course of 4 hours.

3.44 moles of HF are trapped in the wash water.

GC analysis of the crude product gives:

	$\text{CF}_3\text{-CHBrF}$	94.5 %
5	$\text{CF}_2\text{=CFBr}$	3.0 %
	$\text{CF}_2\text{Br-CHF}_2$	1.1 %
	$\text{CF}_3\text{-CHF}_2$	< 1.0 %

356 g of crude product were collected in the trap. The yield of  $\text{CF}_3\text{-CHBrF}$  is about 93% of theory, relative to the  $\text{CF}_2\text{=CFBr}$  reacted. The purified crude product was characterized by IR and NMR measurements and also by determination of the boiling point of +7 to 7.5°C.

#### Example 8

15 For the hydrofluorination of trifluoriodo-ethylene, which can be prepared, for example, by dehydrochlorinating 2-chloro-1,2,2-trifluoro-1-iodo-ethane by known methods, the experimental apparatus of Example (1), filled with the catalyst of Example (1), is used. A total of 249 g (1.20 moles) of  $\text{CF}_2\text{=CFI}$  and 46 g (2.3 moles) of HF (corresponding to a molar ratio  $\text{CF}_2\text{=CFI:HF}$  of 1:1.9) are passed through the reactor at a temperature of 140 to 146°C, in the course of 4.5 hours.

25 1.03 moles of HF are determined in the wash water by titration. GC analysis of the crude condensate gives the following composition:

$\text{CF}_3\text{-CHF}_2$	93.5 %
$\text{CF}_2\text{=CFI}$	2.5 %
$\text{CF}_3\text{-CHF}_2$	1.1 %

$\text{CF}_2\text{I}-\text{CHF}_2$	1.0 %
$\text{CF}_2\text{I}-\text{CF}_2\text{I}$	< 1 %

The crude product trapped weighs 268 g; the resulting yield of  $\text{CF}_3-\text{CHF}_2$  is thus about 94% of theory, 5 relative to the  $\text{CF}_2=\text{CFI}$  reacted. The resulting main product was further characterized by IR,  $^{19}\text{F}$  and  $^1\text{H}$  NMR measurements. The boiling point of the ethane is  $+39^\circ\text{C}/1$  bar.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the preparation of very pure fluorine-containing ethanes of the general formula  $\text{CF}_3\text{-CHXY}$ , in which X denotes H or F and Y denotes H, F, Cl, Br or iodine, from fluorine-containing ethylenes of the general formula  $\text{CF}_2\text{=CXY}$ , in which X and Y have the meaning indicated above, with at least the equimolar amount of hydrogen fluoride, in the gas phase, which process comprises carrying out the reaction at temperatures of 20-200°C and in the presence of a chromium oxyfluoride catalyst which has been treated with hydrogen fluoride and elemental fluorine.
2. A process as claimed in claim 1, wherein the chromium oxyfluoride catalyst has been pre-treated with a gas mixture containing fluorine and hydrogen fluoride.
3. A process as claimed in claim 1 or 2 which comprises carrying out the reaction at reaction temperatures of 40°-190°C.
4. A process as claimed in claim 1 or 2 which comprises carrying out the reaction at reaction temperatures of 60°-180°C.
5. A process as claimed in claim 1 or 2 wherein the molar ratio of fluorine-containing ethylene to hydrogen fluoride is 1:1 to 1:3.

FETHERSTONHAUGH & CO.  
OTTAWA, CANADA

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